

# THE REPRESENTATION OF HIGHLY NON-IDEAL PHASE EQUILIBRIA USING COMPUTER GRAPHICS

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THE CONSIDERABLE ENHANCEMENT to the teaching of thermodynamic phase equilibria achieved through the use of computer graphics has recently been shown by Naik *et al* [1] for the two simplest classes of phase behavior, as classified by Scott and Van Konynenburg [2,3]. In this paper we extend the work reported in [1] to include the considerably more non-ideal phase behavior shown by classes III, IV and V. Thus, at Cornell, we are now able to allow all five classes of phase equilibria to be displayed on Evans and Sutherland multipicture system II vector refresh workstations, with the full range of interactive manipulation of the display described in [1]. Currently the programs are being used by 120 students in five courses, with great success.

## METHOD OF DATA GENERATION

For these more complex systems, the representation of the phase diagram (the pressures, temperatures and compositions) was obtained from the Soave

TABLE 1.  
Parameters Used for the Generation of the Phase Diagrams

$\omega$  is Pitzer's acentric factor;  $\theta$  and  $\zeta$  are combining rule parameters for the potential energy and size [8].

	$T_c$ , K	$P_c$ , atm	$\omega$	$\theta$	$\zeta$
CLASS III					
Component 1	190.6	45.4	0.008	0.013	0.01
Component 2	373.2	88.2	0.100	—	—
CLASS IV					
Component 1	282.4	49.7	0.085	-0.017	0.00
Component 2	588.0	62.3	0.346	—	—
CLASS V					
Component 1	588.0	62.3	0.346	-0.042	0.00
Component 2	272.4	49.7	0.085	—	—

The three-dimensional phase diagrams, involving pressure, temperature and composition axes, are depicted as wire-frame objects enclosed within a normalized cube. The liquid regions are shown as continuous lines . . . the vapor regions are depicted as dashed lines.

[4] modification of the Redlich-Kwong equation of state. The non-linear equations involved in this approach were solved using a Marquardt [5] algorithm, available in Argonne National Laboratories' MINPAK software package. The critical lines originating from these mixtures were calculated using a method proposed by Heidemann and Khalil [6]. It should be noted that the parameters used for the generation of the different classes (III, IV and V) do not correspond to real systems; they are simply sufficient to generate the phase diagram typifying a particular class of behavior. These parameters are given in Table 1.

## GRAPHICAL REPRESENTATION OF THE PHASE DIAGRAMS

The three-dimensional phase diagrams, involving pressure, temperature and composition axes, are depicted as wire-frame objects enclosed within a normalized cube. The liquid regions are shown as continuous lines while the vapor regions are depicted by dashed lines. Solid lines are also used to present the pure component vapor lines and the critical lines. The critical points of the pure components are highlighted as bright dots.

**Class III** - Class III systems exhibit the most complicated phase equilibria; there are several sub-divisions of this class which include liquid-liquid and gas-gas immiscibility. The most interesting sub-class is the one in which the critical line originating at the critical point of the less volatile component exhibits both a maximum and a minimum in pressure. Systems which are classified as being Class III also show a

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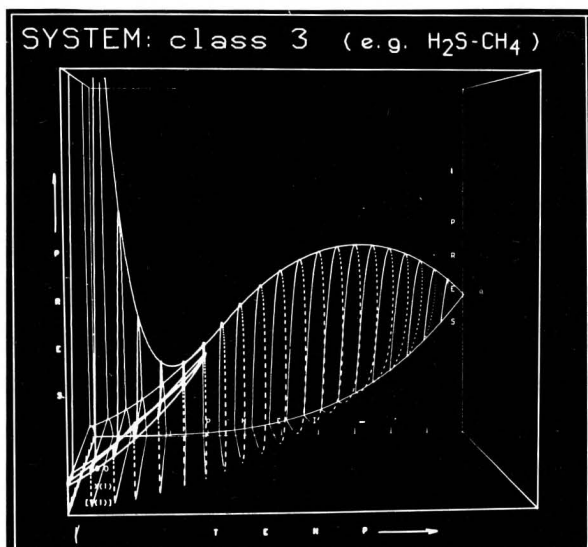


FIGURE 1

second, short, critical line which originates at the critical point of the more volatile component.

Figure 1 gives a clear presentation of the sigmoidal behavior of the critical line which originates at the critical point of the less volatile component. Figure 2 shows the same phase diagram from a different angle superimposed with a low-temperature isothermal cut. In this figure the temperature of the cut is within the three-phase region and thus a three-phase tie-line is present. Isobaric and constant composition cuts can also be superimposed on the three-dimensional phase diagram.

Any of the aforementioned cuts can be seen as a two-dimensional plot instead of being superimposed on the diagram. A series of such plots is shown in

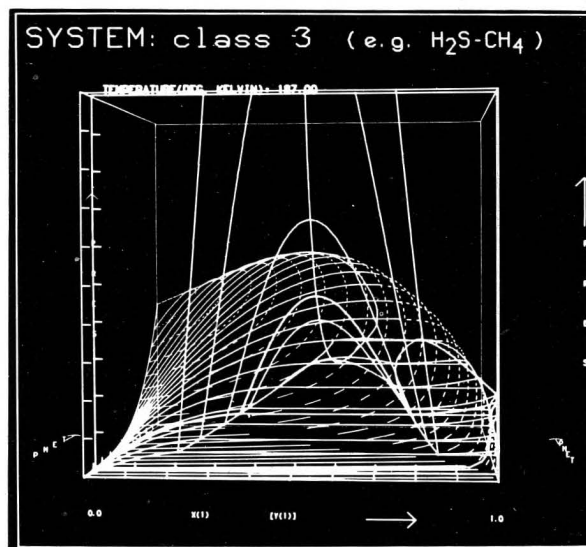
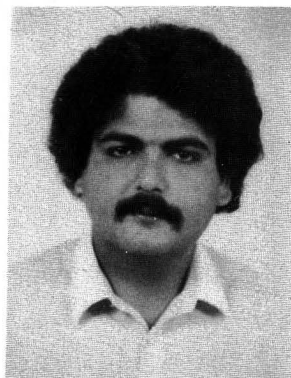


FIGURE 2

Figure 3. The ability of the software to allow a continuous set of cuts to be taken can be used to good effect to demonstrate the transition between different phenomena. Figures 3 (a)-(d) show the transition of the isobaric cuts in the vicinity of the minimum of the critical lines which originates at the critical point of the less volatile component. Figure 3(a) shows a Tx cut at high pressure; Figure 3(b) shows another cut at a pressure very close to the minimum; Figure 3(c) represents a cut just below the minimum and Figure 3(d) completes the series with a cut at a still lower pressure.

**Class IV** - Systems in this class are characterized by three critical lines and two regions of liquid-liquid immiscibility. The first critical line is short and ex-

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tends from the critical point of the more volatile component to an Upper Critical End Point. The second critical line is longer; it originates at the critical point of the less volatile component, goes through a maximum in pressure and terminates at a Lower Critical End Point. The Lower Critical End Point and Upper Critical End Point enclose one liquid-liquid immiscibility region. The third critical line appears at the low-temperature, low-pressure region of the system. The relationship between Classes IV and III can be seen by comparing Figure 4 and Figure 1; in Class IV the long critical line intersects the three-phase region, whereas in Class III it does not. Figure 5 shows an expanded view of the two liquid-liquid immiscibility regions. One can easily see the critical line intersecting the liquid surface and emerging in a lower pres-

sure region. Some three-phase tie-lines are also shown.

**Class V** - Class V systems are similar to the ones in Class IV, but they lack the low-temperature, low-pressure critical line and liquid-liquid immiscibility. Actually, Class V systems would emulate Class IV behavior if the solid phase did not extend to sufficiently high temperatures and pressure to intersect with the fluid phase emergence of the critical line [7]. Figures 6 and 7 show the phase diagram for this class from two different views. Figure 7 also shows a constant composition cut superimposed on the three-dimensional phase diagram.

#### SUMMARY

The extension of our previous work [1] to the more

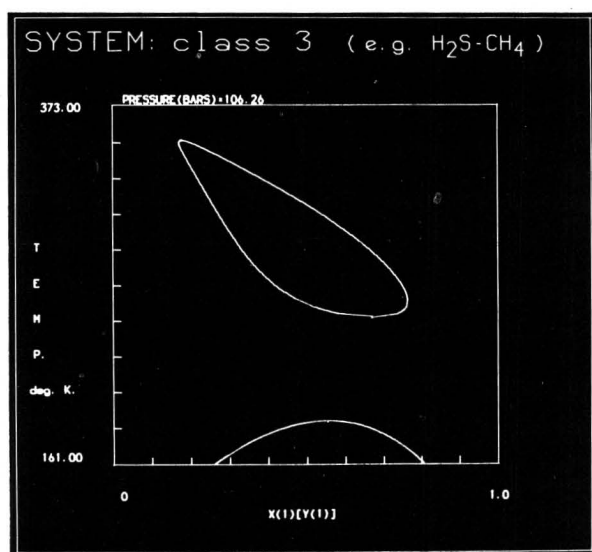


FIGURE 3a

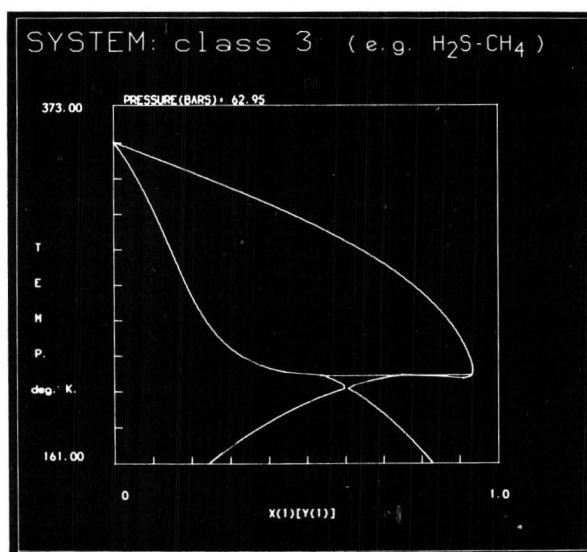


FIGURE 3c

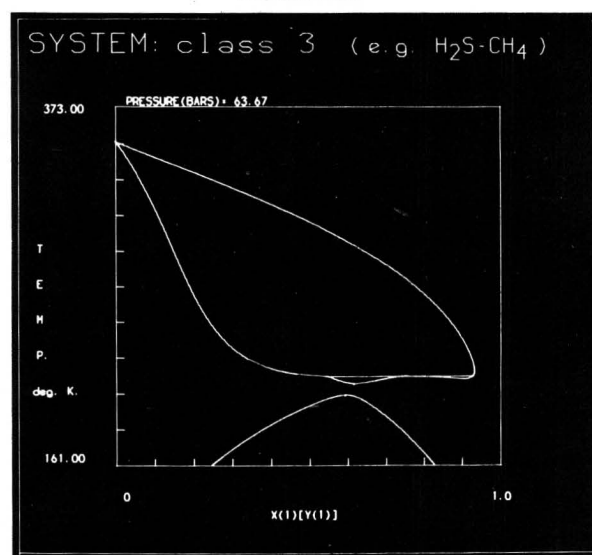


FIGURE 3b

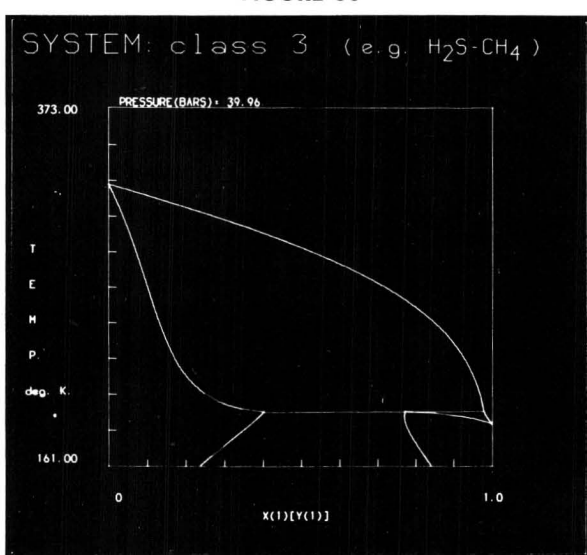


FIGURE 3d

complex Classes III, IV and V permits us to provide complete coverage of all the most commonly encountered types of phase behavior, with all the benefits that an interactive software package on a sophisticated computer graphics system can provide. Student and instructor response to their inclusion in both undergraduate and graduate level courses has been overwhelmingly positive. We feel that this approach provides the key to a significant improvement in the teaching of this difficult subject.

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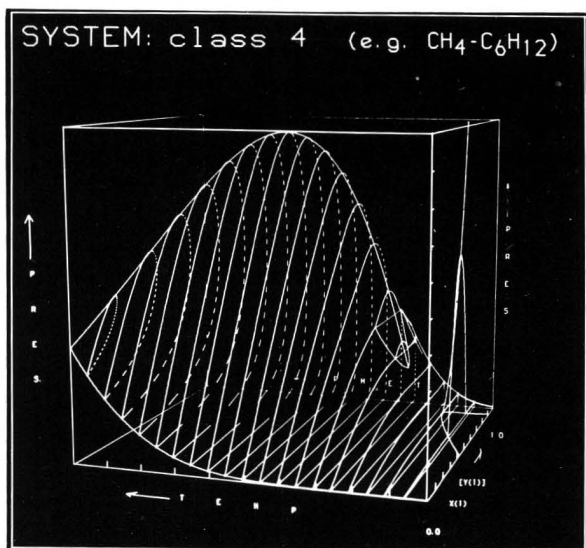


FIGURE 4

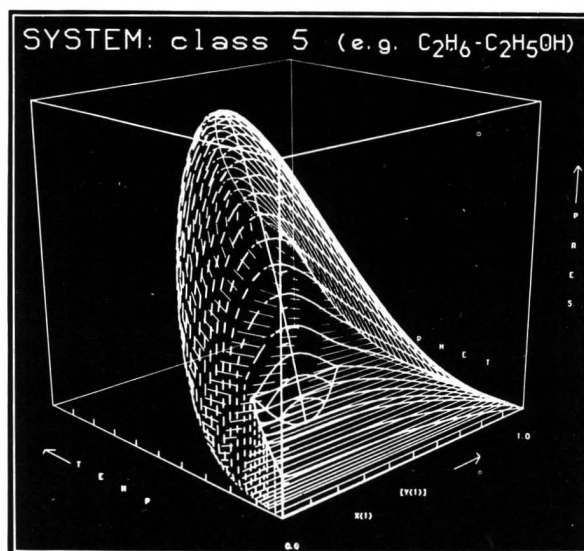


FIGURE 6

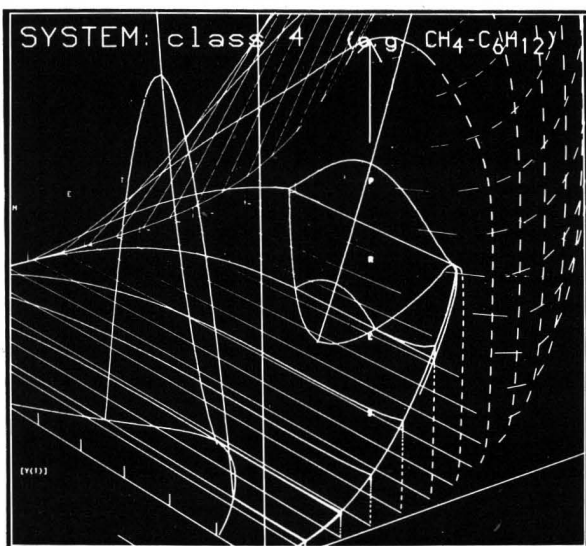


FIGURE 5

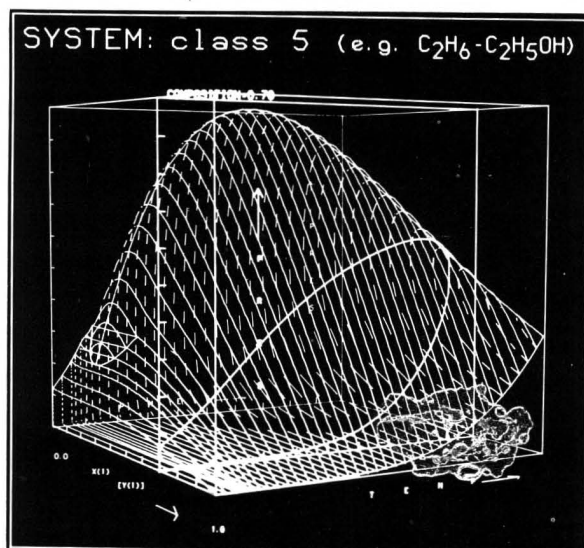


FIGURE 7